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Sputter-Coated Microparticle Additives for Tailored Optical Properties

by Daniel M Baechle and Delaney M Jordan

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14. ABSTRACT
Many bulk materials have coatings on them for protection and durability, and much of this comes in the form of paint as it is easy to apply and much cheaper to replace than the part that it covers. If the properties of the paint can be controlled, then any surface can be easily modified to suit particular needs. This study focused on the development of thin film sputter-deposited coatings on particles for use as additives to modify the optical reflectance and absorbance spectra of the bulk material. First, modeling software was used to predict what material combinations and thicknesses would produce the optical reflectance spectra for a given color. In this study, silicon films of varying thickness were modeled on top of a thin copper film to tailor the desired properties. Following modeling, the designed deposition was tested on a flat silicon wafer and analyzed using Rutherford backscattering spectrometry and spectrophotometry. Finally, the coatings were sputter-deposited onto 127-micron-diameter silica spheres and analyzed for color and uniformity. Once the desired optical properties have been demonstrated, they will be incorporated into a polymer matrix for further testing.

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fluidized bed, thin film, microparticles, coating, sputter deposition, CVD

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Contents

List of Figures

List of Tables

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1. Introduction

The US Army Research Laboratory (ARL) has previously demonstrated magnetron sputter deposition onto a vibro-fluidized bed as a viable method for coating millions of small particles with thin films of metals, ceramics, and multilayered materials.[1] This is a practical method for the batch production of microparticles with tailored optical, physical, and electromagnetic properties, which are useful in the additive industry for modifying bulk polymer and composite materials. Previous research has demonstrated the ability to control the reflectance and absorbance of a flat surface using thin film layers of metals and dielectrics, based on the principle of thin film interference.[2–4] ARL's previous studies have also demonstrated the ability to use these techniques to produce multicolored microspheres in a single batch, although precise control of microsphere color was not demonstrated.

In this study, magnetron sputtering is used to coat microparticle spheres with thin film metallic and dielectric layers to tailor their optical spectra. Computer modeling and deposition onto flat substrates are used to predict and control the final color of the microspheres. Fluidization of the particle bed is achieved through the same shaking mechanism as in Baechle et al.[1] using an external electromagnetic shaker. The results of elemental analysis on the flat wafer coatings are discussed, along with reasons for differences between the predicted and measured spectral data. Once coatings with the desired optical properties were demonstrated on flat wafers, they were produced on beds of glass microspheres with an average diameter of 127 μm. The microspheres were then analyzed using scanning electron microscopy (SEM), Rutherford backscattering spectrometry (RBS), and optical microscopy.

2. Experiment

The iterative process for the development of each coating morphology included modeling the thin film design, optimizing it on a flat wafer substrate, and replicating the final design on the silica particles. Modeling was performed using The Essential MacLeod software package (Thin Film Center, Inc.) to find material combinations and layer thicknesses that would produce an optical spectra of interest (i.e., different reflectance values at different wavelengths). All designs focused on thin film layers less than 100 nm thick using materials that were already present in the sputter target library, such as aluminum (Al), copper (Cu), and silicon (Si). These design considerations, along with limiting the number of layers, were made to ensure reasonable deposition times; the microspheres have such a high combined surface area that sputtering a thick coating or depositing many layers would require prohibitively long sputtering times. The initial design for a red coating consisted of

a glass substrate with a 65-nm-thick Cu layer, followed by an 8-nm-thick Si layer. The modeled blue/purple coating consisted of a 65-nm-thick Cu layer followed by a 15-nm-thick Si layer. These initial modeled designs can be seen in Fig. 1. Although these coatings do not produce sharp transitions in reflectance, they were chosen to demonstrate the ability to control color with just 2 very thin layers.

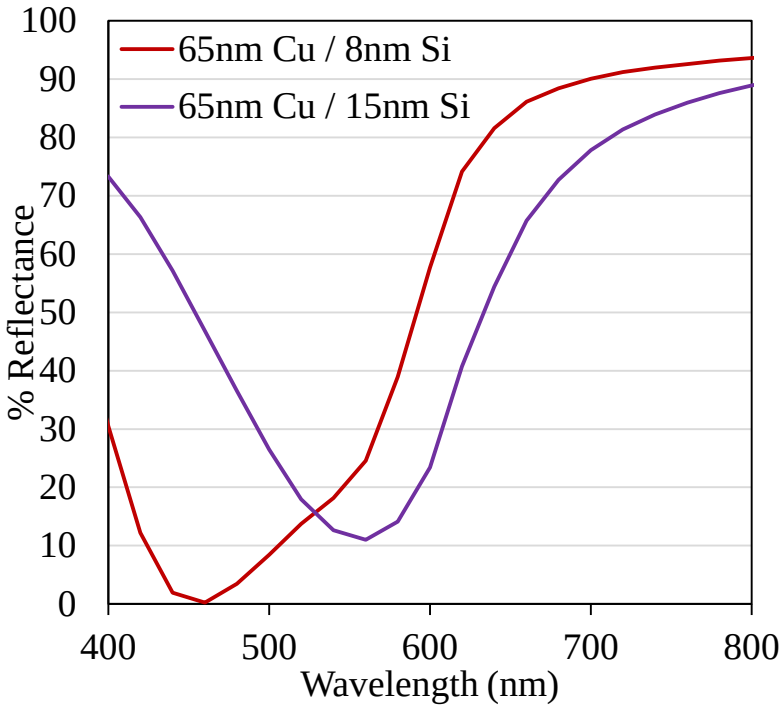

Fig. 1 Modeled reflectance of the Cu-Si coatings

Once the layers of the model had been adjusted to give a peak reflectance value in a given range of wavelengths and a minimum elsewhere, the layers of the design were sputter deposited onto a flat Si wafer substrate. The sputter deposition system consisted of an approximately 45- × 45- × 60-cm vacuum chamber (Sharon Vacuum) and two 3-inch magnetrons (Onyx 3, Angstrom Sciences), as illustrated in Fig. 2. After loading the substrate into the vacuum chamber, we evacuated the chamber to a base pressure of 1.0–5.0 µTorr using a turbopump (TMU521P, Pfeiffer). Argon gas flow into the chamber was set at 27 sccm using a mass flow controller (AX-MC-200SCCM-D, Apex), giving a working pressure of 1.0 mTorr while the turbopump ran at 549 Hz. Cu was deposited using a DC power supply (MDX500, Advanced Energy) at a power of 60 W for 10 min. The Si layers were deposited using an RF power supply (RFX600, Advanced Energy), at 60 W for 10 min for the red coating and 80 W for 7.5 min for the blue/purple coating. These experimental parameters can be seen in Table 1. Although a higher power would have resulted in faster deposition times, this value was chosen to avoid overheating and damaging the sputter target and gun during the long sputter depositions that

will later be used to coat the particles. The target-to-substrate working distance was 130 mm, which was chosen to center the substrate position between the 2 sputter guns. In the front view of Fig. 2 the sputter heads are angled with respect to the sample stage. This configuration allows co-sputtering and multilayer coating without having to move the sample stage or particle bed between different sputter head positions.

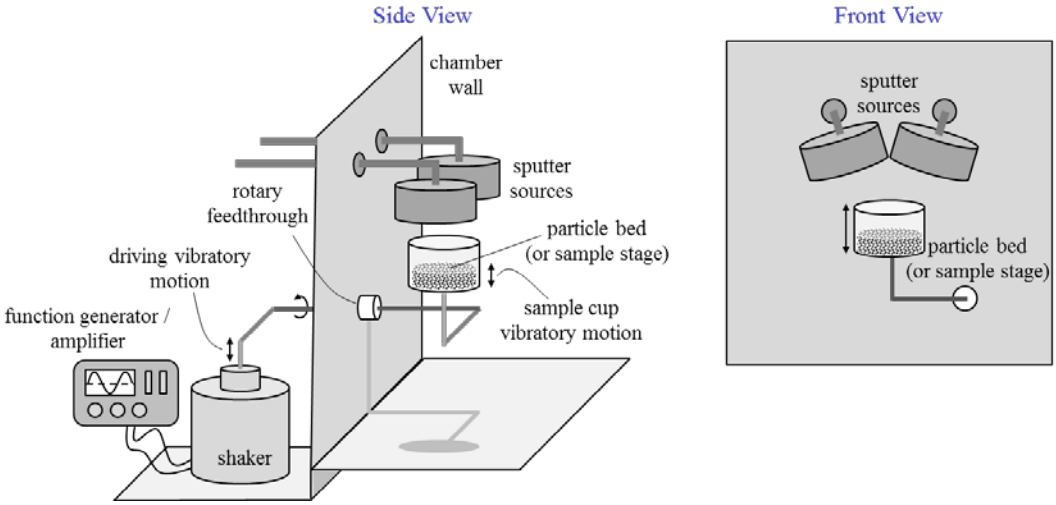

Fig. 2 Schematic of the sputter system

Table 1 Sputter parameters for flat samples

Sample	Cu sputter power (W)	Cu sputter time (min)	Si sputter power (W)	Si sputter time (min)
Red wafer	60	5	60	10
Blue wafer	60	5	80	7.5

Deposition onto a flat surface enabled fast design optimization and allowed analysis that would be difficult to perform on the small, curved surface of the microspheres. All wafers were placed in the chamber with a smaller piece of an Si wafer overlapping to serve as a mask. Analysis of the coatings on the flat substrates included RBS (5SDH-2, National Electrostatics) for coating thickness, X-ray photoelectron spectroscopy (XPS, Physical Electronics Versaprobe 2) depth profiling for elemental analysis, and spectrophotometry (Perkin Elmer UV/vis/NIR spectrometer Lamda 1050) for reflectance of the coatings in the visible spectrum. Coating thickness, as measured by RBS, was used to calculate the deposition rate onto a flat surface and the particle bed.

Once the desired color was demonstrated on the flat substrates, the coatings were duplicated on glass microspheres (SIO2PSL12000, Fiber Optic Center, Inc.), seen

in Fig. 3. The microspheres were initially sieved to a size range of 105–150 μm, and a 10-g sample was placed in a 9-cm-diameter, 1-cm-tall petri dish. The dish was installed 130 mm under the sputter heads, as illustrated in Fig. 2. Sputter time to deposit the desired thickness of the coatings on the microspheres was determined using the following formula, derived in Baechle et al.[1]:

$$\dot{t}_p = \dot{t}_f \frac{\pi \rho_p r_p r_c^2}{3 m_p^T}. \quad (1)$$

Fig. 3 Plain glass microspheres, 105–150 μm

Here, $\dot{t}_p$ is the deposition rate onto the particle bed (meters per second), $\dot{t}_f$ is the deposition rate onto a flat surface (meters per second, determined from the flat substrate deposition thickness and duration), ρ_p is the density of the particle material (glass), r_p is the microsphere radius, r_c is the radius of the petri dish, and m_p^T is the total mass of the particle bed. Because of the large surface area of the particle beds, deposition times for Cu and Si were on the order of hours, as can be seen in Table 2. Shaking frequency and amplitude were tuned to produce the desired fluidization behavior by visually inspecting the bed. Fluidization parameters can be seen in Table 2. The same sputter process for the flat substrates described previously (vacuum, gas flow) was used for deposition onto the particles. After deposition, coating thickness on the microspheres was determined using RBS. Beam spot size for RBS was approximately 3 mm, providing an average measurement over hundreds of microspheres. Spectrophotometry was performed using a 150-mm InGaAs integrating sphere module. The microspheres were mounted on a 25-mm-diameter piece of carbon tape, and the beam spot was the same size. The reflectance of the carbon tape was also measured separately. Image analysis (ImageJ, NIH) revealed that approximately 70%–71% of the carbon tape was covered by the microspheres. Thus, 30% of the carbon tape reflectance signal was subtracted from the measured reflectance of the microspheres on the carbon tape.

Table 2 Sputter parameters for microsphere samples

Sample	Size (mm)	Initial sample mass (g)	Shaking frequency (Hz)	Cu sputter power (W)	Cu sputter time (min)	Si sputter power (W)	Si sputter time (min)
Red spheres	105–150	11.16	38.8	60	195	60	510
Blue spheres	105–125	10.01	45.8	60	195	80	510

3. Results and Discussion

Coating thicknesses, as measured by RBS, can be seen in Table 3. RBS indicated the presence of oxygen in the films, with the red Si film having more oxygen than the blue Si film. Although the chamber was checked with a helium leak detector, smaller leaks and outgassing of the chamber walls may have contributed to the oxygen content in these films. As seen in Fig. 4, the "red" wafer has a color gradient from red to orange, and the "blue" wafer from blue to purple. The gradients are likely due to the angle of the sputter head with respect to the substrate. In Fig. 4, a black circle marks the approximate location and size of the measured area for XPS and spectrophotometry.

Table 3 RBS measured coating layer thicknesses

Sample	Cu layer thickness (nm)	Si layer thickness (nm)
Red wafer	65.6	20.0
Blue wafer	64.8	20.0
Red spheres	30.0	10.7
Blue spheres	30.0	19.5

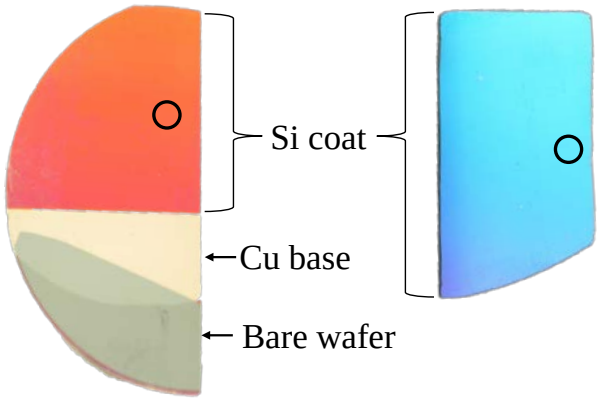

Fig. 4 Red (left) and blue (right) coated wafers

Spectrophotometry results for the red and blue wafers can be seen in Fig. 5. XPS indicated that the red coating (in the spot seen in Fig. 4) was approximately 63% elemental Si and 37% SiO_2. XPS indicated that the sampled spot on the blue coating was 91% elemental Si and 9% SiO_2. XPS depth analysis showed that oxygen was primarily concentrated at the surface of the coatings. Neither XPS nor RBS detected oxygen content in the Cu layer. The reflectance models were revised to include oxidized layers in the aforementioned ratios and are also presented in Fig. 5. In the revised models, SiO_2 layers were placed at the free surface of the coating. Finer-scale series layering of Si and SiO_2 layers did not affect the modeled reflectance. In both cases, the Si layers are thicker than initially modeled but still produced the desired colors. The revised model still tends to overpredict reflectance below 500 nm in the red coating and overpredict reflectance across the spectrum for the blue coating. These results are likely due to the material models included in the Essential MacLeod software not entirely matching the as-sputtered materials.

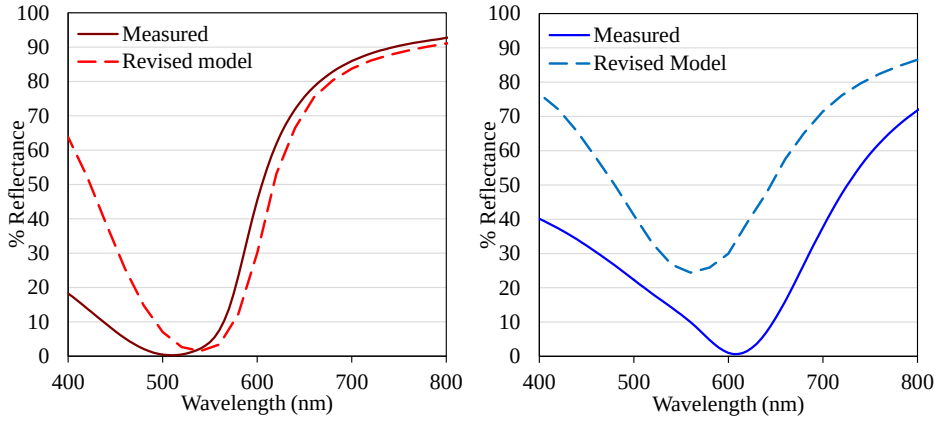

Fig. 5 Measured reflectance spectra and revised models for red (left) and purple (right) wafers

The coating thicknesses of the red and blue microspheres as measured using RBS can be found in Table 3. RBS measurements indicated oxygen present in both Si coatings, but to a greater extent in the red coating. Cu coating thickness was about half of that expected, possibly due to the particle bed shifting to one side of the petri dish during coating, thus reducing the area of particles presented to the sputter flux at any given moment. An image of the Cu-coated particles can be seen in Fig. 6.

Fig. 6 Cu-coated glass microspheres

Images of the coated spheres can be seen in Fig. 7. To the naked eye, the spheres appear a uniform color. However, as seen in Fig. 7, a microscopic examination reveals varying shades and colors. Nevertheless, the color uniformity is much better than previously reported.[1] Previous experiments found a correlation between particle size and color within a coated batch of mixed-size particles.[1] Other researchers have shown that different size particles will segregate within a particle bed when agitated, with larger particles tending to rise to the top of the bed.[5] Therefore, it is expected that a particle bed with a narrower size distribution will have a more uniform color when coated using this process. However, spacer or calibration grade glass microspheres with less than 10% difference in diameter are prohibitively expensive for quantities over 10 g. Polymer microspheres with high size uniformity can be found for extremely low prices because of their bulk use in the cosmetics industry. However, polymer microspheres quickly melt in the present system. An active cooling system for the particle bed may allow coating of inexpensive polymer microspheres, but providing sufficient cooling to a moving bed of microspheres in a vacuum may be difficult or impossible. Thus, for a scalable solution, there will likely be a tradeoff between cost and spectral response.

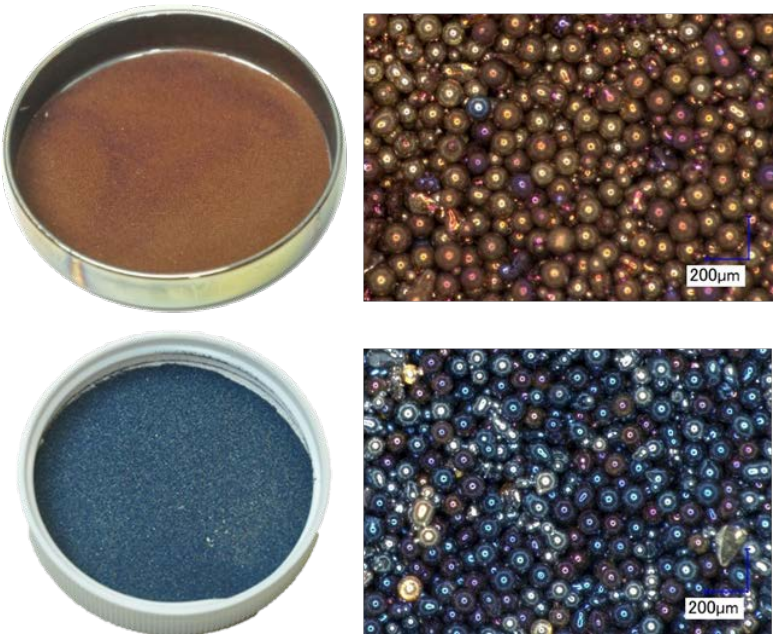

Fig. 7 Images of the red (top) and blue (bottom) microspheres

SEM images of the red and blue microspheres can be seen in Fig. 8. Representative particles are shown. The coating appears uniform across all particles in a sample. However, small (~1 µm) protrusions appear on the surface of all particles. The exact source of the protrusions is unknown, but they may be flecks of coating chipped off of other particles or the sides of the petri dish, or dust present in the uncoated particles.

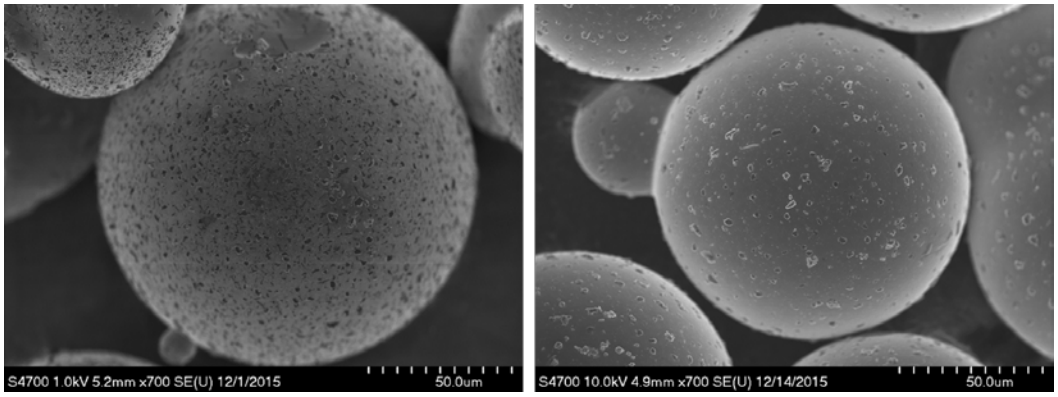

Fig. 8 SEM images of red (left) and blue (right) microspheres

Reflectance spectra of the microspheres can be seen in Fig. 9. The measured reflectance of the spheres is much lower than that of the flat coatings. Scattering off of the spherical surfaces and coating roughness likely contribute to the low measured reflectance values. Shaking amplitude and sputter power were kept low to avoid creating surface roughness, but some roughness is unavoidable in this

process because of the mechanical agitation of the particles. Coating roughness was generally better than previous experiments,[1] but not as good as a flat, static substrate. The thin Cu coating also likely reduced the reflectance magnitude in the red and near-IR regions. Future coatings could use a thicker Cu layer to increase reflectance in these regions.

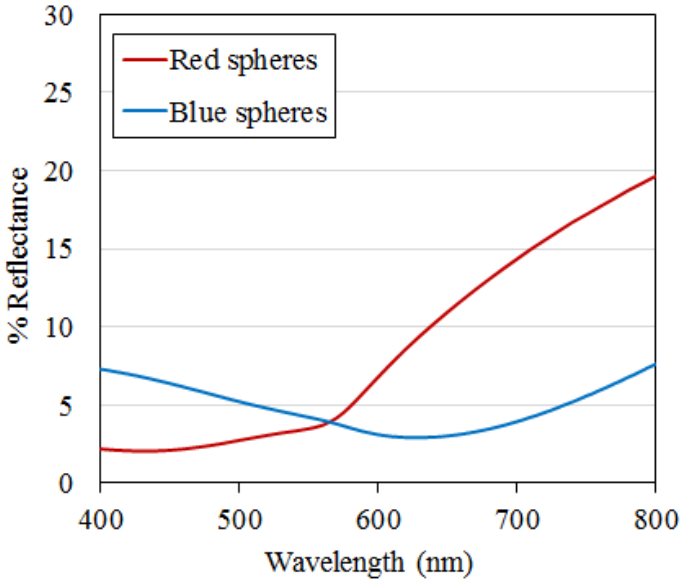

Fig. 9 Measured reflectance of the red and blue spheres

4. Summary and Conclusions

These experiments demonstrated the ability to model, produce, and characterize sputtered coatings for tailored reflectance in the visible spectrum on flat substrates and fluidized beds of 105- to 125-μm glass microspheres. The measured reflectance of the coatings did not exactly match the models because of the unanticipated levels of oxygen in the coatings. However, the expected colors were still produced using the system. Future experiments could develop an ARL library of reflectance measurements of sputtered films to feed more representative reflectance values into the Essential MacLeod software. In its present state, the software is still a useful tool for estimating reflected color of sputtered films. Even with no detectable leaks, oxygen is expected at some level in the coatings on microspheres because of the large surface area of the microsphere bed and thus slow effective deposition rate onto the microspheres (tens of nanometers per hour at best). The microspheres coated in this work will be incorporated into a polymer matrix for composite and large-area coating applications. Future experiments will seek to improve reflectance magnitude and demonstrate different designed reflectance peaks on smaller particles.

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List of Symbols, Acronyms, and Abbreviations

Al	aluminum
ARL	US Army Research Laboratory
Cu	copper
DC	direct current
RBS	Rutherford backscattering spectrometry
RF	radio frequency
sccm	standard cubic centimeters per minute
SEM	scanning electron microscopy
Si	silicon
XPS	X-ray photoelectron spectroscopy

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